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SU-SEL-72-012

**Fundamental Studies of the Metallurgical,
Electrical, and Optical Properties of
Gallium Phosphide and Gallium
Phosphide Alloys**

April 1972

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**Technical Summary Report
Covering the Period
1 February 1969 through 31 January 1972**

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Prepared under

National Aeronautics and Space Administration
Grant No. NGL 05-020-043

**SOLID-STATE ELECTRONICS LABORATORY
STANFORD ELECTRONICS LABORATORIES
STANFORD UNIVERSITY • STANFORD, CALIFORNIA**



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FUNDAMENTAL STUDIES OF THE METALLURGICAL, ELECTRICAL, AND OPTICAL PROPERTIES OF GALLIUM PHOSPHIDE AND GALLIUM PHOSPHIDE ALLOYS

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FOREWORD

The studies presented began on 1 February 1969 and were concluded on 31 January 1972. The research activity was conducted under the supervision of Professor Gerald L. Pearson at the Solid-State Electronics Laboratory at Stanford University who was also the Program Manager. A three-month, no-cost extension to April 30, 1972 was requested in order to provide sufficient time for preparation of the final report.

This is the Final Technical Documentary Report of the work under Grant No. NGL 05-020-043.

SU-SEL-72-012

FUNDAMENTAL STUDIES OF THE METALLURGICAL, ELECTRICAL,
AND OPTICAL PROPERTIES OF GALLIUM PHOSPHIDE AND
GALLIUM PHOSPHIDE ALLOYS

ABSTRACT

This report summarizes the research carried out under Grant No. NGL 05-020-043. The program on the grant was directed toward the following separate projects related to the metallurgical, electrical, and optical properties of gallium phosphide and gallium phosphide alloys:

- (1) Diffusion of Sulfur in Gallium Phosphide and Gallium Arsenide.
- (2) Properties of Gallium Phosphide Schottky Barrier Rectifiers for Use at High Temperatures.

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Chapter I

INTRODUCTION

This report summarizes the technical activity supported at Stanford University by National Aeronautics and Space Administration Grant No. NGL 05-020-043 during the 36 month period from 1 February 1969 through 31 January 1972. The program of this grant was directed toward the following separate projects related to the metallurgical, electrical, and optical properties of III-V compound semiconductor materials and devices:

- (1) Diffusion of Sulfur in Gallium Phosphide and Gallium Arsenide
- (2) Properties of Gallium Phosphide Schottky Barrier Rectifiers for Use at High Temperatures.

A detailed technical report was prepared for each of these projects so that only the abstracts are included in this summary report together with a complete bibliography of all published papers (with abstracts) and oral presentations generated by these projects.

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Chapter II

DIFFUSION OF SULFUR IN GALLIUM PHOSPHIDE AND GALLIUM ARSENIDE

Abstract

The diffusion of substitutional impurities in III-V compounds has usually been explained in the literature by a model of vacancy diffusion within a single sublattice. Experimental evidence for this model, however, has been obtained solely from measurements of the temperature variation of the diffusion coefficient.

In the work reported here, a radiotracer technique was used to study the diffusion of sulfur, a substitutional donor impurity, in GaP and GaAs as a function of temperature, sulfur pressure, component pressure, and background doping of the host crystal. The importance of uniquely defining the experimental conditions has been stressed, and the necessity of elucidating diffusion mechanisms in compound semiconductors by determining the quantitative dependence of diffusion coefficient on component pressure has been emphasized. Previous reports in the literature concerning sulfur diffusion in GaAs have been inadequate in both of these respects. The diffusion of sulfur in GaP has not been reported previously.

The results reported here indicate that the variation of the diffusion coefficient with component pressure for sulfur in both GaP and GaAs is not in agreement with the model of vacancy diffusion within a single sublattice. The diffusion coefficient of sulfur in GaP was found to be independent of phosphorus pressure, whereas the diffusion coefficient of sulfur in GaAs varied as $(P_{As4})^{\frac{1}{2}}$ at low arsenic pressures, and appeared to saturate at arsenic pressures greater than 0.5-1 atmospheres. The results for sulfur in GaP are consistent with diffusion via the di-

vacancy $V_{Ga} - V_P$, while the diffusion of sulfur in GaAs can be explained by movement via the gallium divacancy $V_{Ga} - V_{Ga}$. A review of the literature indicated that the failure of the sublattice model to explain the dependence of impurity diffusion on component pressure may be a general phenomenon in III-V compounds.

The variation of solubility in III-V compounds with impurity vapor pressure has, with few exceptions, been ignored in the literature. The results reported here indicate that the dependence of surface concentration on sulfur vapor density for both GaP and GaAs is not in agreement with the usual model of incorporation of sulfur atoms on isolated anion sites. Possible reasons for this discrepancy are discussed.

Incremental Hall and plasma reflection methods were used to study the electrically active part of the impurity distribution in the diffused layers. At high concentrations, a large concentration of the sulfur was found to be electrically inactive at room temperature. This observation is of practical importance since previous reports in the literature concerning sulfur diffusion in GaAs have often assumed complete ionization of the impurities in the diffused layer. Diffusion coefficients calculated using this assumption may be in error.

The above abstract is from the Ph.D. thesis of A.B.Y. Young as given in Report Su-SEL-69-017, Stanford Electronics Laboratories, Stanford, California, March 1969. One published paper (A.B.Y. Young and G.L. Pearson, *J. Phys. Chem. Solids* 31, pp. 517-527, 1970) originated from this work. Dr. Young is now employed at Fairchild Semiconductor, Palo Alto, California.

Chapter III

PROPERTIES OF GALLIUM PHOSPHIDE SCHOTTKY BARRIER RECTIFIERS

Abstract

Gallium phosphide Schottky barrier rectifiers for operation above 400°C were developed and tested. Single crystal GaP was grown from a Ga-rich melt by vertical liquid phase epitaxy techniques on heavily ($2 \times 10^{17} \text{ cm}^{-3}$) Te-doped (111) oriented GaP substrates. The carrier concentration of the epitaxial material, as determined by capacitance-voltage measurements, varied by two orders of magnitude between runs with the lowest value obtained being $3 \times 10^{15} \text{ cm}^{-3}$.

A study of metal-GaP systems at elevated temperatures was made to determine suitable metals for Schottky barrier and ohmic contacts. Films of Al, Ag, or Ni formed reliable high temperature Schottky barriers on GaP with alloying not occurring until 635 , 690 , and 760°C respectively. For ohmic contact to the n-type substrate, Ag based compositions such as Ag-Ge, Ag-Te, and Ag-Te-Sb covered with Ni were heat treated at temperatures between 600 and 700°C . The composite Ag films were consistently ohmic and stable above 500°C . The lowest specific contact resistance on GaP reported to date, amounting to $4 \times 10^{-4} \text{ ohm-cm}^2$, was obtained with the Ag-Te-Sb system. Applying these results to simple GaP structures (using a Ni Schottky barrier and an Ag-Te-Ni ohmic contact) produced rectifiers with a 200 volt breakdown voltage which could be operated at temperatures above 400°C .

Simple Schottky barrier devices exhibited high forward resistances and were not protected from the environment. Therefore, a photolithographically-etched planar structure was developed to control the surface

at the interface and at the perimeter of the contact. These diodes were passivated with a 3000 \AA layer of SiO_2 to insure stability and low leakage currents. The ohmic contact throughout was Ag-Te-Ni whereas several Schottky barrier metals including Al, Cr-Au, and Cr-Ag were examined.

The principal analytical tool used in the evaluation of the planar Schottky barrier devices was the scanning electron microscope. By this means, and in conjunction with voltage-current measurements and temperature tests in a helium atmosphere, microalloying, and reverse voltage breakdown were observed. Regions of high resistivity which contribute to the residual high forward resistance were detected at the Schottky barrier interface using the induced conductivity mode of the scanning electron microscope. Consequently, a new metal system (Cr-Ag) was developed and shown to be an excellent GaP Schottky barrier at temperatures in excess of 400 $^{\circ}\text{C}$. This study resulted in rectifying devices which operate at a reverse breakdown of 200 V and forward current density of 325 $\text{\AA}/\text{cm}^2$.

The above abstract is from the Ph.D. thesis of A.J. Domenico as given in Report SU-SEL-71-061, Stanford Electronics Laboratories, Stanford, California, March 1972. Three published papers (J.S. Harris, Y. Nannichi, G.L. Pearson, and G.F. Day, *J. Appl. Phys.* 40, pp. 4575-4581 (1969); H. Nakatsuka, A.J. Domenico, and G.L. Pearson, *Solid-State Electronics* 14, pp. 849-853 (1971)) originated from this work. Dr. Domenico is now employed at Litronix, Cupertino, California.

Chapter IV

ABSTRACTS OF PUBLICATIONS RESULTING FROM THIS GRANT

1. "Zinc Diffusion into Gallium Phosphide Under High and Low Phosphorus Pressures," S.F. Nygren and G.L. Pearson, *J. Electrochem. Soc.* 116, pp. 648-654 (1969).

The acceptor zinc has been diffused into n-type single crystal gallium phosphide at temperatures between 700 and 1000°C from diffusion sources which lie in two different regions of the Ga-P-Zn phase diagram. One source (pure zinc) provides low phosphorus overpressure and leads to p-n junctions which are distinctly nonplanar. The other (zinc plus excess phosphorus) provides high phosphorus overpressure and leads to smaller diffusion coefficients and considerably more planar p-n junctions. These effects are consistent with the interstitial-substitutional model for diffusion of zinc in GaP. With either source, diffusion induced dislocations are formed throughout the diffused layer after an incubation time. The p-n junction depth corresponding to the first appearance of the induced dislocations is found to be greater when the high phosphorus pressure source is used.

2. "Ohmic Contacts to Solution-Grown Gallium Arsenide," J.S. Harris, Y. Nannichi, G.L. Pearson, and G.F. Day, *J. Appl. Phys.* 40, p pp. 4574-4581 (1969).

A study has been made on the properties of Ohmic contacts to single-crystal n-type GaAs wafers which were grown by liquid epitaxy techniques. Carrier concentration profiles at the n⁺-n junctions were measured by the Schottky barrier capacitance technique for

both Au-Ge-Ni alloyed contacts and liquid epitaxial n+ contacts. The frequently observed high resistance layers at the interface were eliminated by the contacting processes described here. The ohmic contact problems and the results of other experiments are explained in terms of the GaAs binary phase diagram and non-stoichiometry considerations.

3. "Diffusion of Sulfur in Gallium Phosphide and Gallium Arsenide," A.B.Y. Young and G.L. Pearson, *J. Phys. Chem. Solids* 31, pp. 517-527 (1970).

A radiotracer technique was used to study the diffusion of sulfur in GaP and GaAs as a function of temperature, sulfur pressure, and component pressure. The results reported here indicate that the variation of diffusion coefficient with component pressure for sulfur in both GaP and GaAs is not in agreement with a model of vacancy diffusion within a single sublattice. The diffusion coefficient of sulfur in GaP was found to be independent of phosphorus pressure, whereas the diffusion coefficient of sulfur in GaAs varied as $(P_{As_4})^{\frac{1}{2}}$ at low arsenic pressures, and appeared to saturate at arsenic pressures greater than 0.5-1 atm. The results for sulfur in GaP are consistent with diffusion via the divacancy ($V_{Ga}V_P$) while the diffusion of sulfur in GaAs can be explained by movement via the gallium divacancy ($V_{Ga}V_{Ga}$). The apparent decrease in the diffusion coefficient at high sulfur concentrations can be qualitatively explained by the formation of the complex ($V_{Ga}S_3$). A plasma reflection technique was used to study the electrically active part of the sulfur-diffused layers in GaAs. At high sulfur concentrations a large percentage of

the sulfur in the diffused layer was found to be electrically inactive. This phenomenon is suggested as a possible explanation for the large discrepancy among previously reported values of the diffusion coefficient of sulfur in GaAs.

4. "Ohmic Contacts to n-Type GaP Devices for Use at High Temperatures," H. Nakatsuka, A.J. Domenico, and G.L. Pearson, Jap. Soc. Appl. Phys. 40, pp. 58-60 (1972).

The specific contact resistance of n-type GaP-metal contact was calculated by the thermionic-field-emission theory. Alloying temperatures of Au, Al, Ag, and Ni films evaporated on GaP single crystals were measured at $520^{\circ}\text{C} \pm 20^{\circ}\text{C}$, $635^{\circ}\text{C} \pm 20^{\circ}\text{C}$, $690^{\circ}\text{C} \pm 20^{\circ}\text{C}$, and $760^{\circ}\text{C} \pm 20^{\circ}\text{C}$, respectively. Ag-Ge, Ag-Te, and Ag-Te-Sb contacts covered with Ni films showed ohmic characteristics when heated at temperatures between 600°C and 700°C and were found to be stable well above 500°C . Current-voltage characteristics at various ambient temperatures were measured.

5. "Improved Ohmic Contacts to n-Type GaP Devices," H. Nakatsuka, A.J. Domenico, and G.L. Pearson, Solid-State Electronics 14, pp. 849-853 (1971).

Ohmic contacts to n-type GaP devices which are capable of operation at ambient temperatures as high as 500°C were investigated. Alloying temperatures of Au, Al, Ag, and Ni films on GaP single crystals were measured and found to be 520, 635, 690, and 760°C respectively, within an accuracy of $\pm 20^{\circ}\text{C}$. Films of Ag covered with Ni showed good wetting on GaP and were stable well above 500°C .

Silver based alloy contacts such as Ag-Ge, Ag-Te, and Ag-Te-Sb covered with Ni films were ohmic after heat treatments at temperatures between 600 and 700°C. The lowest specific contact resistance obtained to date is $4 \times 10^{-4} \Omega \text{ cm}^2$ with the Ag-Te-Sb system.

Chapter V

ORAL PRESENTATIONS RESULTING FROM THIS GRANT

1. "Ohmic Contacts to n-Type GaP Devices for Use at High Temperatures," H. Nakatsuka, The Second Conference on Solid-State Devices, Tokyo, Japan, September 1970.
2. "Metallurgical, Electrical, and Optical Properties of Column III-V Solid Solutions," G.L. Pearson, Technical University of Denmark, Lyngby, Denmark, September 1971; P.N. Lebedev Institute of Physics, Moscow, USSR, September 1971; Institute of Inorganic Chemistry, Novosibirsk, USSR, September 1971; A.F. Joffe Physico-Technical Institute, Leningrad, USSR, October 1971; University of Tokyo, Tokyo, Japan, October 1971.